

# Crystallographic and spectroscopic characterization of 5-chloropyridine-2,3-diamine

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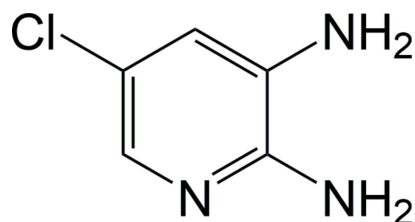
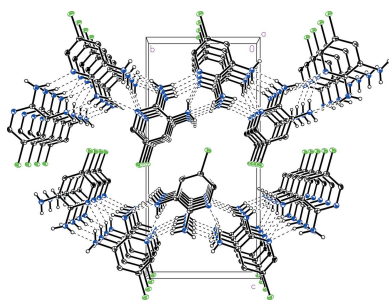
Edited by L. Fabian, University of East Anglia, England

**Keywords:** crystal structure; hydrogen bonding;  $\pi$ -stacking.**CCDC reference:** 1562267**Supporting information:** this article has supporting information at journals.iucr.org/e

The two *ortho*-amino groups of the title compound, C<sub>5</sub>H<sub>6</sub>ClN<sub>3</sub>, twist out of the plane of the molecule to minimize intramolecular interaction between the amino hydrogen atoms. In the crystal, the amino groups and the pyridine N atom engage in intermolecular hydrogen bonding. The molecules pack into spiral hydrogen-bonded columns with offset face-to-face  $\pi$ -stacking.

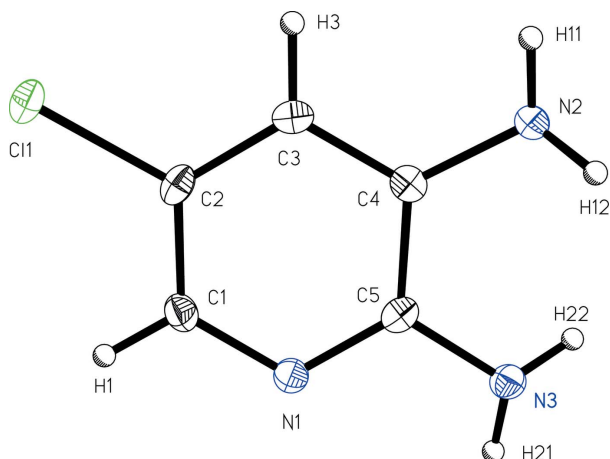
## 1. Chemical context

The title compound, 5-chloropyridine-2,3-diamine, is a tri-substituted pyridine featuring *ortho*-amino groups and a chlorine atom. While all of the sixteen isomers of 5-chloropyridine-2,3-diamine are commercially available, none of their crystal structures have been reported in the literature. 5-Chloropyridine-2,3-diamine may be produced by nitrating 2-amino-5-chloropyridine with nitric acid to give 2-amino-3-nitro-5-chloropyridine, which is then reduced with sodium dithionite (Israel & Day, 1959). The reduction may also be accomplished with hydrogen gas and Pd/C (Xie *et al.*, 2016). 5-Chloropyridine-2,3-diamine has proven useful as a reagent in complex syntheses, such as in the synthesis of aldose reductase inhibitors with antioxidant activity (Han *et al.*, 2016), the regioselective functionalization of imidazopyridines *via* alkylation catalyzed by a Pd/Cu catalyst (Baladi *et al.*, 2016), the preparation of amino acid oxidase inhibitors (Xie *et al.*, 2016), the preparation of  $\beta$ -glucuronidase inhibitors (Taha *et al.*, 2016), the preparation of imidazopyridine derivatives with activity against MCF-7 breast adenocarcinoma (Püsküllü *et al.*, 2015) and the preparation of dihydroxyarene-substituted benzimidazoles, quinazolines and larger rings *via* cyclocondensation of diamines (Los *et al.*, 2012).



## 2. Structural commentary

The molecular structure of the title compound 5-chloropyridine-2,3-diamine (Fig. 1) shows that the molecule is nearly planar with r.m.s deviation from the mean plane of all non-hydrogen atoms of 0.013 (3) Å. The amino groups *ortho* and



**Figure 1**  
A view of 5-chloropyridine-2,3-diamine (I) with the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

*meta* to the pyridine nitrogen atom twist out of the plane of the molecule in such a way as to minimize contact with one another, with  $\text{NH}_2$  plane to molecular plane angles of  $45(3)$  and  $34(3)^\circ$  for N2 and N3, respectively. It is notable that the achiral title compound crystallizes in a non-enantiogenic (Söhncke) space group, although not a polar space group.

### 3. Supramolecular features

Notable intermolecular interactions observed in the structure of 5-chloropyridine-2,3-diamine (I) include  $\text{N}_{\text{amine}}-\text{H}\cdots\text{N}_{\text{pyr}}$  and  $\text{N}_{\text{amine}}-\text{H}\cdots\text{N}_{\text{amine}}$  hydrogen bonding interactions and offset face-to-face  $\pi$ -stacking. The molecules connect into a one-dimensional strip running parallel to the crystallographic

**Table 1**  
Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

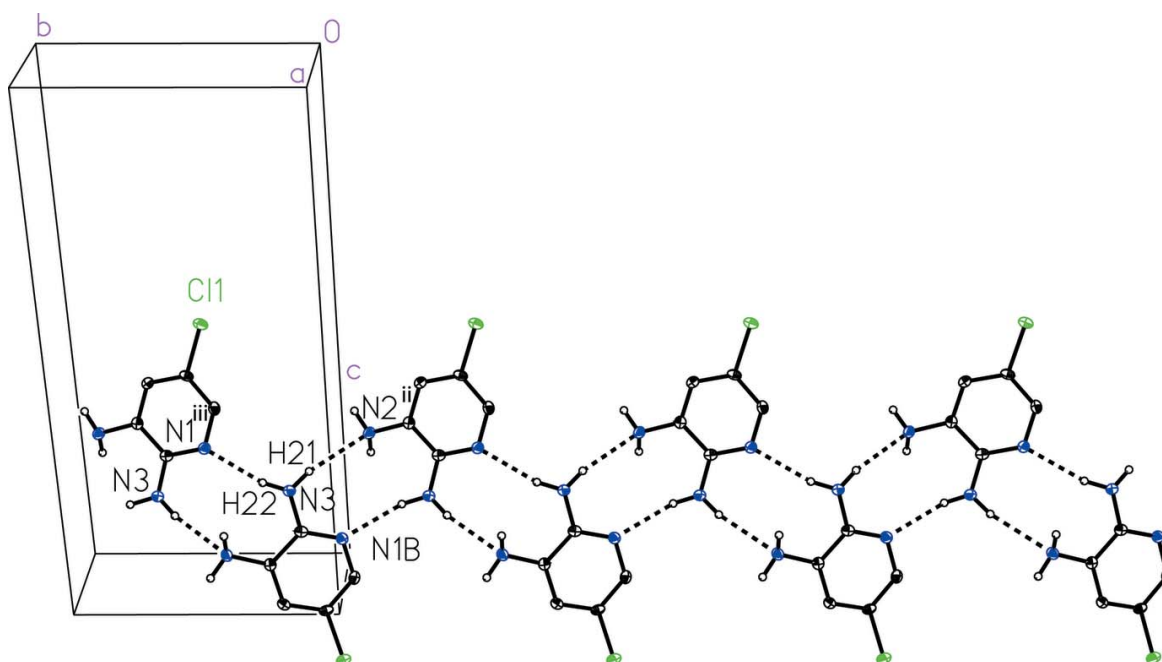
$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N2}-\text{H12}\cdots\text{N1}^{\text{i}}$	0.86 (2)	2.48 (3)	3.264 (3)	151 (3)
$\text{N3}-\text{H21}\cdots\text{N2}^{\text{ii}}$	0.89 (2)	2.38 (2)	3.250 (4)	166 (3)
$\text{N3}-\text{H22}\cdots\text{N1}^{\text{iii}}$	0.90 (2)	2.19 (2)	3.075 (4)	167 (3)

Symmetry codes: (i)  $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$ ; (ii)  $-x+2, y-\frac{1}{2}, -z+\frac{3}{2}$ ; (iii)  $-x+2, y+\frac{1}{2}, -z+\frac{3}{2}$ .

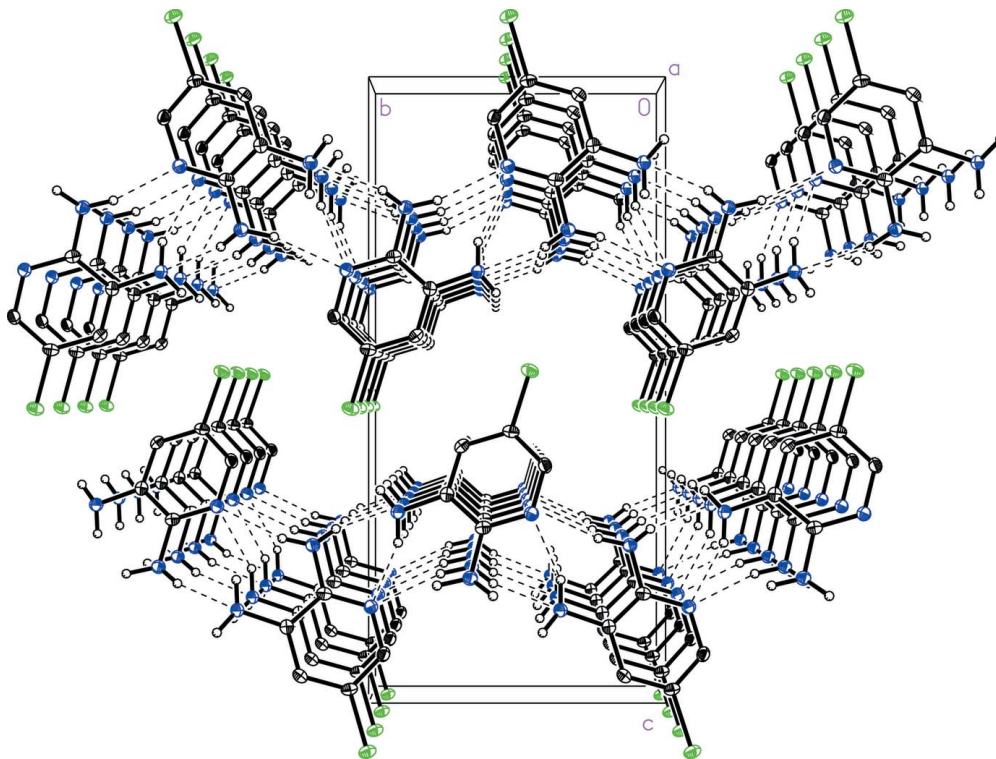
*b* axis (Fig. 2) with long  $\text{N3}_{\text{amine}}-\text{H21}\cdots\text{N2}^{\text{ii}}_{\text{amine}}$  [symmetry code (ii)  $-x+2, y-\frac{1}{2}, -z+\frac{3}{2}$ ] and  $\text{N3}_{\text{amine}}-\text{H22}\cdots\text{N1}^{\text{iii}}_{\text{pyr}}$  [symmetry code (iii)  $-x+2, y+\frac{1}{2}, -z+\frac{3}{2}$ ] hydrogen bonding interactions with donor-acceptor distances of 3.250 (4) and 3.075 (4)  $\text{\AA}$ , respectively (Table 1). A third  $\text{N}_{\text{amine}}-\text{H}\cdots\text{N}_{\text{pyr}}$  hydrogen-bonding contact and offset face-to-face  $\pi$ -stacking can be seen to extend along the crystallographic *a* axis (Fig. 3), acting to link the one-dimensional strips into two-dimensional sheets. The  $\text{N2}_{\text{amine}}-\text{H12}\cdots\text{N1}^{\text{i}}_{\text{pyr}}$  [symmetry code (i)  $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$ ] contact exhibits a donor-acceptor distance 3.264 (3)  $\text{\AA}$ . The  $\pi$ -stacking is characterized by a centroid-to-centroid distance of 3.756 (1)  $\text{\AA}$ , plane-to-plane distances of 3.414 (2)  $\text{\AA}$  and a ring offset of 1.568 (3)  $\text{\AA}$  (Hunter & Saunders, 1990; Lueckheide *et al.*, 2013). Alternatively, the three hydrogen-bonding contacts and the  $\pi$ -stacking taken together can be seen to form a spiral of 5-chloropyridine-2,3-diamine (I) molecules extending along the *a*-axis direction (Fig. 4).

### 4. Database survey

The Cambridge Structural Database (Groom *et al.*, 2016) contains about fifty structurally similar compounds to 5-chloropyridine-2,3-diamine (I), with 2-amino-5-chloropyridine

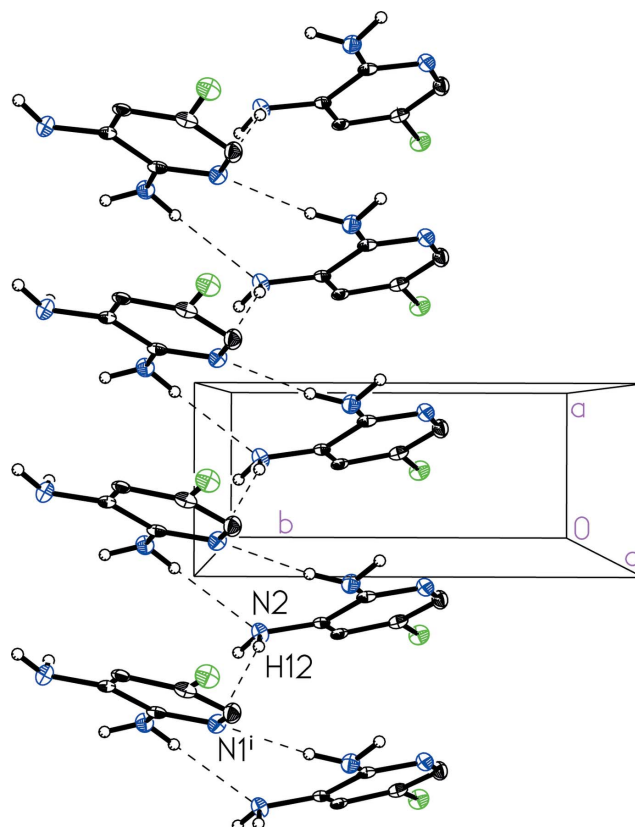


**Figure 2**  
A view of the intermolecular  $\text{N3}_{\text{amine}}-\text{H21}\cdots\text{N2}^{\text{ii}}_{\text{amine}}$  and  $\text{N3}_{\text{amine}}-\text{H22}\cdots\text{N1}^{\text{iii}}_{\text{pyr}}$  one-dimensional hydrogen bonding in 5-chloropyridine-2,3-diamine (I). [Symmetry codes: (ii)  $-x+2, y-\frac{1}{2}, -z+\frac{3}{2}$ ; (iii)  $-x+2, y+\frac{1}{2}, -z+\frac{3}{2}$ ]


**Figure 3**

A view of the packing in 5-chloropyridine-2,3-diamine (I) indicating hydrogen bonding connecting the one-dimensional strips into two-dimensional sheets along with offset face-to-face  $\pi$ -stacking.

(AMCLPY12) (Pourayoubi *et al.*, 2007) and 2-amino-3-chloropyridine (URAXER) (Hu *et al.*, 2011) being the most chemically and structurally similar. The C—Cl bond length in the title compound, with distance 1.748 (3) Å, is comparable to those in 2-amino-5-chloropyridine (AMCLPY12) and 2-amino-3-chloropyridine (URAXER), with distances 1.7404 (14) and 1.735 (3) Å, respectively. The C—N<sub>amine</sub> distances in the title compound, 1.406 (4) and 1.385 (4) Å, however, are somewhat longer than in 2-amino-5-chloropyridine (AMCLPY12) [1.3602 (19) Å] and 2-amino-3-chloropyridine (URAXER) [1.351 (4) Å]. 2-amino-5-chloropyridine (AMCLPY12), which does not have the *meta*-NH<sub>2</sub> substitution of the title compound, packs in a herringbone formation featuring centrosymmetric head-to-tail N<sub>amine</sub>—H···N<sub>pyr</sub> hydrogen bonding dimers with donor–acceptor distance 3.031 (2) Å. 2-Amino-3-chloropyridine (URAXER), has a *meta*-Cl substitution in place of the *meta*-NH<sub>2</sub> in the title compound. Like 2-amino-5-chloropyridine (AMCLPY12), 2-amino-3-chloropyridine (URAXER) features a herringbone packing with centrosymmetric head-to-tail N<sub>amine</sub>—H···N<sub>pyr</sub> hydrogen-bonded dimer with a similar donor–acceptor distance of 3.051 (5) Å. The similar hydrogen-bonding motif in these two related compounds differs from the title compound, which does not exhibit centrosymmetric hydrogen-bonding dimerization. 2-Amino-3-chloropyridine (URAXER) also has short intermolecular Cl···Cl interactions of 3.278 (3) Å, where no such short halogen–halogen contact was observed in 2-amino-5-chloropyridine (AMCLPY12) or the title compound.


**Figure 4**

A view of the spiral hydrogen-bonded chain in 5-chloropyridine-2,3-diamine (I) highlighting the N2<sub>amine</sub>—H12···N1<sup>i</sup><sub>pyr</sub> contact. [Symmetry code: (i)  $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$ .]

## 5. Synthesis and crystallization

5-Chloropyridine-2,3-diamine (97%) was purchased from Aldrich Chemical Company, USA. A single crystal suitable for analysis was selected from the purchased sample and used as received.

## 6. Analytical data

$^1\text{H}$  NMR (Bruker Avance 400 MHz, DMSO  $d_6$ ):  $\delta$  4.99 (*br s*, 2 H,  $\text{NH}_2$ ), 5.55 (*br s*, 2 H,  $\text{NH}_2$ ), 6.69 (*d*, 1 H,  $J = 2.3$  Hz,  $\text{C}_{\text{aryl}}\text{H}$ ), 7.21 (*d*, 1 H,  $J = 2.3$  Hz,  $\text{C}_{\text{aryl}}\text{H}$ ).  $^{13}\text{C}$  NMR ( $^{13}\text{C}\{^1\text{H}\}$ , 100.6 MHz, DMSO  $d_6$ ):  $\delta$  116.58 ( $\text{C}_{\text{aryl}}\text{H}$ ), 118.38 ( $\text{C}_{\text{aryl}}$ ), 131.32 ( $\text{C}_{\text{aryl}}$ ), 131.66 ( $\text{C}_{\text{aryl}}\text{H}$ ), 147.10 ( $\text{C}_{\text{aryl}}$ ). IR (Thermo Nicolet iS50, ATR,  $\text{cm}^{-1}$ ): 3392 (*m*, N–H *str*), 3309 (*m*, N–H *str*), 3172 (*m*, aryl C–H *str*), 1637 (*s*, aryl C=C *str*), 1572 (*m*), 1472 (*s*), 1421 (*m*), 1347 (*w*), 1307 (*w*), 1280 (*w*), 1240 (*m*), 1068 (*m*), 939 (*w*), 887 (*w*), 861 (*m*), 792 (*m*), 770 (*m*), 680 (*s*), 630 (*s*), 568 (*s*), 490 (*s*), 449 (*s*). GC/MS (Hewlett-Packard MS 5975/GC 7890):  $M^+$  = 143 (calc. exact mass = 143.03).

## 7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on carbon were included in calculated positions and refined using a riding model with C–H = 0.95 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  of the aryl C-atoms. The positions of the four amino hydrogen atoms were found in the difference map and they were refined semi-freely using a distance restraint  $d(\text{N–H}) = 0.91$  Å, and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ .

## Acknowledgements

This work was supported by Vassar College. X-ray facilities were provided by the US National Science Foundation (grants Nos. 0521237 and 0911324 to JMT). NMR facilities were provided by the US National Science Foundation (grant No. 1526982 to JMT and TG). We acknowledge the Salmon Fund of Vassar College for funding publication expenses.

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**Table 2**  
Experimental details.

Crystal data	
Chemical formula	$\text{C}_5\text{H}_6\text{ClN}_3$
$M_r$	143.58
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	125
$a, b, c$ (Å)	3.7565 (8), 8.7002 (17), 18.350 (4)
$V$ (Å <sup>3</sup> )	599.7 (2)
$Z$	4
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	0.53
Crystal size (mm)	0.10 × 0.05 × 0.04
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 2013)
$T_{\text{min}}, T_{\text{max}}$	0.75, 0.98
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	14989, 1845, 1477
$R_{\text{int}}$	0.087
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.714
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.041, 0.084, 1.07
No. of reflections	1845
No. of parameters	94
No. of restraints	4
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.37, -0.38
Absolute structure	Flack $x$ determined using 511 quotients $[(I^+) - (I^-)] / [(I^+) + (I^-)]$ (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	0.01 (6)

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *SHELXT2014* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *SHELXTL2014* (Sheldrick, 2008), *OLEX2* (Dolomanov *et al.*, 2009) and *Mercury* (Macrae *et al.*, 2008).

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Xie, D., Lu, J., Xie, J., Cui, J., Li, T.-F., Wang, Y.-C., Chen, Y., Gong, N., Li, X.-Y., Fu, L. & Wang, Y.-X. (2016). *Eur. J. Med. Chem.* **117**, 19–32.

## supporting information

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## Crystallographic and spectroscopic characterization of 5-chloropyridine-2,3-diamine

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### Computing details

Data collection: *APEX2* (Bruker, 2013); cell refinement: *SAINTE* (Bruker, 2013); data reduction: *SAINTE* (Bruker, 2013); program(s) used to solve structure: *SHELXT2014* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *SHELXTL2014* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL2014* (Sheldrick, 2008), *OLEX2* (Dolomanov *et al.*, 2009) and *Mercury* (Macrae *et al.*, 2008).

### 5-Chloropyridine-2,3-diamine

#### Crystal data

$C_5H_6ClN_3$

$M_r = 143.58$

Orthorhombic,  $P2_12_12_1$

$a = 3.7565$  (8) Å

$b = 8.7002$  (17) Å

$c = 18.350$  (4) Å

$V = 599.7$  (2) Å<sup>3</sup>

$Z = 4$

$F(000) = 296$

$D_x = 1.590$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 4306 reflections

$\theta = 2.6$ – $29.7^\circ$

$\mu = 0.53$  mm<sup>-1</sup>

$T = 125$  K

Plate, colourless

$0.10 \times 0.05 \times 0.04$  mm

#### Data collection

Bruker APEXII CCD  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 8.3333 pixels mm<sup>-1</sup>

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(SADABS; Bruker, 2013)

$T_{\min} = 0.75$ ,  $T_{\max} = 0.98$

14989 measured reflections

1845 independent reflections

1477 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.087$

$\theta_{\max} = 30.5^\circ$ ,  $\theta_{\min} = 2.2^\circ$

$h = -5 \rightarrow 5$

$k = -12 \rightarrow 12$

$l = -26 \rightarrow 26$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.041$

$wR(F^2) = 0.084$

$S = 1.07$

1845 reflections

94 parameters

4 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0308P)^2 + 0.2158P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.37$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.38$  e Å<sup>-3</sup>



Absolute structure: Flack  $x$  determined using  
511 quotients  $[(F^-)-(F)]/[(F^+)+(F)]$  (Parsons *et al.*,  
2013)  
Absolute structure parameter: 0.01 (6)

### Special details

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.5035 (2)	0.46707 (8)	0.47194 (3)	0.01872 (16)
N1	0.8538 (6)	0.4647 (3)	0.67658 (12)	0.0148 (5)
N2	0.5894 (7)	0.8717 (3)	0.67694 (14)	0.0153 (5)
H11	0.464 (9)	0.928 (3)	0.6466 (14)	0.018*
H12	0.530 (10)	0.872 (3)	0.7224 (12)	0.018*
N3	0.8976 (7)	0.6490 (3)	0.76777 (13)	0.0154 (5)
H21	1.032 (9)	0.580 (3)	0.7905 (15)	0.018*
H22	0.955 (10)	0.748 (3)	0.7772 (16)	0.018*
C1	0.7608 (8)	0.4231 (3)	0.60820 (16)	0.0157 (6)
H1	0.7977	0.3199	0.5931	0.019*
C2	0.6148 (7)	0.5258 (4)	0.56011 (14)	0.0138 (5)
C3	0.5497 (7)	0.6759 (3)	0.58152 (14)	0.0121 (6)
H3	0.445	0.747	0.5486	0.015*
C4	0.6388 (7)	0.7209 (3)	0.65122 (15)	0.0122 (6)
C5	0.8035 (7)	0.6100 (3)	0.69716 (15)	0.0125 (6)

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cl1	0.0204 (3)	0.0220 (3)	0.0138 (3)	-0.0021 (4)	-0.0034 (3)	-0.0035 (3)
N1	0.0154 (11)	0.0144 (11)	0.0145 (11)	0.0014 (11)	-0.0007 (9)	-0.0001 (11)
N2	0.0182 (14)	0.0137 (12)	0.0140 (11)	0.0036 (9)	-0.0003 (9)	0.0000 (9)
N3	0.0162 (14)	0.0152 (12)	0.0148 (11)	-0.0009 (10)	-0.0036 (9)	0.0004 (10)
C1	0.0176 (15)	0.0126 (14)	0.0171 (14)	0.0008 (11)	0.0014 (12)	-0.0019 (11)
C2	0.0101 (12)	0.0202 (13)	0.0112 (11)	-0.0036 (12)	0.0002 (9)	-0.0016 (12)
C3	0.0061 (14)	0.0157 (12)	0.0146 (12)	-0.0022 (10)	0.0009 (10)	0.0040 (10)
C4	0.0064 (12)	0.0142 (14)	0.0160 (14)	-0.0003 (10)	0.0026 (11)	0.0004 (11)
C5	0.0066 (13)	0.0184 (15)	0.0125 (13)	-0.0017 (11)	0.0021 (10)	0.0011 (11)

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

Cl1—C2	1.748 (3)	N3—H22	0.90 (2)
N1—C5	1.333 (4)	C1—C2	1.371 (4)
N1—C1	1.352 (4)	C1—H1	0.95
N2—C4	1.406 (4)	C2—C3	1.385 (4)

N2—H11	0.88 (2)	C3—C4	1.379 (4)
N2—H12	0.86 (2)	C3—H3	0.95
N3—C5	1.385 (4)	C4—C5	1.423 (4)
N3—H21	0.89 (2)		
C5—N1—C1	118.7 (3)	C1—C2—C11	120.1 (2)
C4—N2—H11	112 (2)	C3—C2—C11	119.7 (2)
C4—N2—H12	111 (2)	C4—C3—C2	119.2 (3)
H11—N2—H12	118 (3)	C4—C3—H3	120.4
C5—N3—H21	115 (2)	C2—C3—H3	120.4
C5—N3—H22	118 (2)	C3—C4—N2	123.0 (3)
H21—N3—H22	114 (3)	C3—C4—C5	117.5 (3)
N1—C1—C2	121.8 (3)	N2—C4—C5	119.4 (3)
N1—C1—H1	119.1	N1—C5—N3	117.5 (3)
C2—C1—H1	119.1	N1—C5—C4	122.5 (2)
C1—C2—C3	120.2 (3)	N3—C5—C4	119.9 (3)
C5—N1—C1—C2	-0.5 (4)	C1—N1—C5—N3	179.3 (2)
N1—C1—C2—C3	-1.7 (4)	C1—N1—C5—C4	3.3 (4)
N1—C1—C2—C11	179.3 (2)	C3—C4—C5—N1	-4.0 (4)
C1—C2—C3—C4	1.0 (4)	N2—C4—C5—N1	179.0 (3)
C11—C2—C3—C4	-180.0 (2)	C3—C4—C5—N3	-179.8 (3)
C2—C3—C4—N2	178.5 (3)	N2—C4—C5—N3	3.2 (4)
C2—C3—C4—C5	1.7 (4)		

## Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H12...N1 <sup>i</sup>	0.86 (2)	2.48 (3)	3.264 (3)	151 (3)
N3—H21...N2 <sup>ii</sup>	0.89 (2)	2.38 (2)	3.250 (4)	166 (3)
N3—H22...N1 <sup>iii</sup>	0.90 (2)	2.19 (2)	3.075 (4)	167 (3)

Symmetry codes: (i)  $-x+1, y+1/2, -z+3/2$ ; (ii)  $-x+2, y-1/2, -z+3/2$ ; (iii)  $-x+2, y+1/2, -z+3/2$ .